

March 23, 1893.

Sir JOHN EVANS, K.C.B., D.C.L., LL.D., Vice-President and Treasurer, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

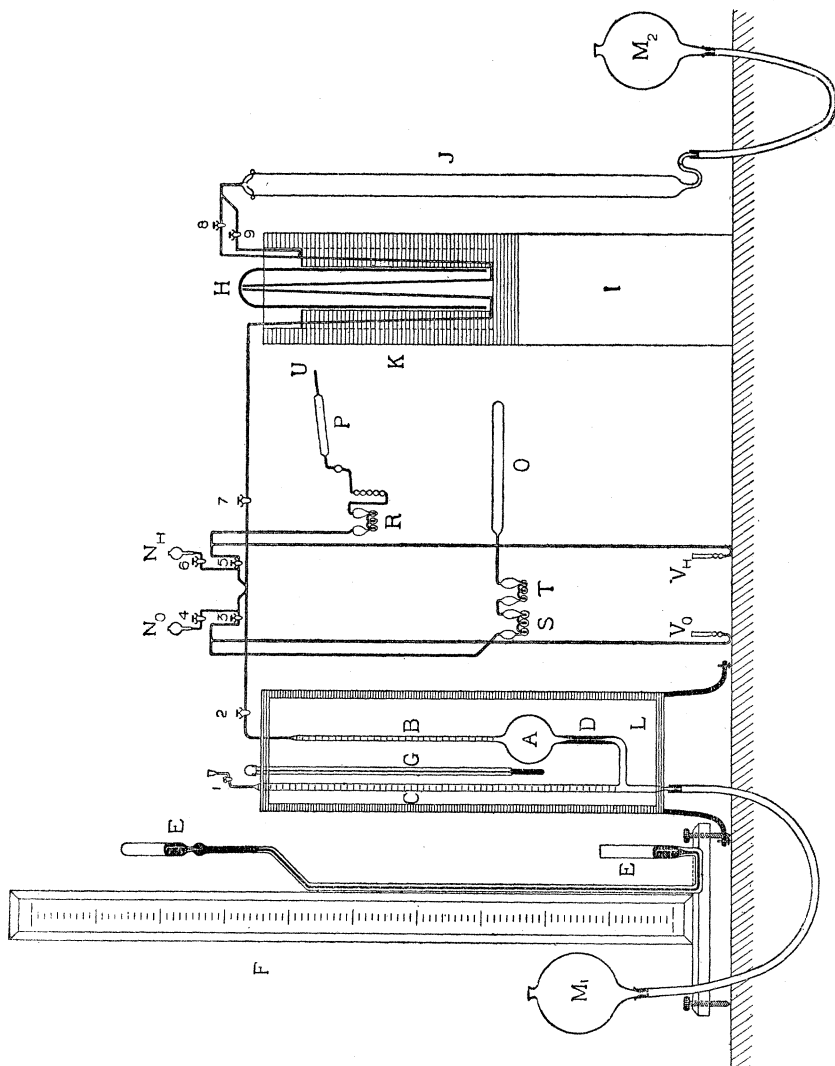
The following Papers were read :—

- I. "On the Composition of Water by Volume." By ALEXANDER SCOTT, M.A., D.Sc., Jacksonian Demonstrator in the University of Cambridge. Communicated by LORD RAYLEIGH, Sec. R.S.\* Received March 4, 1893.

(Abstract.)

In a preliminary note presented to the Society in June, 1887, the results of twenty-one experiments on the composition of water by volume were given in detail. The ratio deduced from these experiments was less than two volumes to one of oxygen. This result was unexpected, because of the greater compressibility of oxygen than of hydrogen, but as every one of the experiments pointed to this result, the evidence for it seemed conclusive. Pursuing the investigation with improved apparatus, especially as regarded making a complete analysis of the residual gas, a serious source of error was discovered in the use of any combustible lubricant for the taps employed. On substituting syrupy phosphoric acid for the vaseline previously employed, the oxides of carbon disappeared as ordinary impurities. In the later experiments two forms of apparatus were employed, the chief difference being that in the earlier form the measuring vessel was not of fixed volume, so that both volume and pressure of the gas had to be measured; in the later form the gas was measured at constant volume by varying the pressure, which alone, therefore, required measurement in each experiment.

As in the apparatus formerly used, the entire apparatus could be completely exhausted of air before beginning an experiment by using the mercury reservoir ( $M_1$ ) and the measuring vessel as a Töppler's pump. The gases were measured in A and B, and after measurement were mixed in the jar H, whence they were drawn into the explosion tube J, and then exploded in fractions till all was used up. The residue was now passed back into H, and then into B, and there measured,



retransferred to J, and expelled through the tap 9 into an absorption tube, and analysed with potassium hydrate and pyrogallol for carbon dioxide and oxygen, and for gases not absorbed by these reagents. These gases were most probably nitrogen, hydrogen, and carbon monoxide (from the absorbents). The mixture thus obtained gave at any rate a *maximum* value for any impurity in the gases employed; when it fell below  $1/110,000$  the gases were considered pure.

The hydrogen required was made from

1. Electrolysis of dilute sulphuric acid.
2. " hydrochloric acid.
3. Action of steam on sodium.
4. Palladium hydride.

The oxygen was obtained from

1. Re-crystallised potassium chlorate.
2. Mercuric oxide.
3. Silver oxide.

All the results in which potassium chlorate was used as the source of the oxygen gave low results, doubtless due to traces of chlorine accompanying the oxygen even after passing through potassium hydrate. The best oxygen was obtained from silver oxide, and the best hydrogen from palladium hydride. The palladium used combined with enough hydrogen to perform twelve experiments in succession. The results of the last series are given in the following table. The oxygen required was obtained from silver oxide.

Column A contains number of experiment.

„ B contains date of experiment.

„ C contains measured volume of hydrogen in grams of mercury.

„ D contains measured volume of oxygen in grams of mercury.

„ E contains excess of hydrogen in grams of mercury.

„ F contains excess of oxygen in grams of mercury.

„ G contains impurity in grams of mercury.

„ H contains number of volumes of hydrogen which unite with one of oxygen.

A.	B.	C.	D.	E.	F.	G.	H.
XXV	Ap. 1	6863·8	3443·8	..	15·4	0·3	2·0020
XXVI	„ 1	6870·0	3432·9	..	2·1	0	2·0024
XXVII	„ 2	6870·1	3439·7	..	9·2	0	2·0026
XXVIII	„ 4	6848·7	3422·1	..	2·9	0	2·0030
XXIX	„ 4	6792·5	3386·6	13·5	..	0	2·0022
XXX	„ 5	6809·2	3399·5	1·5	..	0	2·0025
XXXI	„ 6	6793·9	3399·6	..	7·7	0	2·0029
XXXII	„ 6	6789·6	3389·5	2·9	..	0	2·0023
XXXIII	„ 7	6808·5	3396·4	6·0	..	0	2·0028
XXXIV	„ 8	6793·1	3395·8	..	2·1	0	2·0017
XXXV	„ 8	6786·5	3395·0	..	5·4	0	2·0022
XXXVI	„ 9	6814·8	3411·9	..	9·3	0	2·0028

Mean =  $2\cdot00245 \pm 0\cdot00007$ .

The mean of all the experiments in the variable volume apparatus, and in which potassium chlorate was the chief source of oxygen, is

$$\begin{array}{l} 2\cdot000903 \pm 0\cdot00004 \text{ impurity equally distributed in both gases,} \\ 1\cdot99925 \pm 0\cdot00005 \quad \text{,,} \quad \text{assumed to be all in hydrogen,} \end{array}$$

in 5 series of 19 experiments in all.

The mean of all the experiments in the constant volume apparatus, in which silver oxide was used as the source of the oxygen, and sodium and steam either directly, or after absorption in palladium for the hydrogen, is

$$\begin{array}{l} 2\cdot002435 \pm 0\cdot00006 \text{ impurity in both gases equally,} \\ \text{or} \quad 2\cdot002431 \pm 0\cdot00006 \quad \text{,,} \quad \text{hydrogen alone.} \end{array}$$

This is the mean of 53 experiments in 5 series.

If 6 experiments be rejected we get the value

$$2\cdot002466 \pm 0\cdot000003$$

as the result of 47 experiments in 5 series, and any impurity makes no difference, whether it be assumed all in the hydrogen or equally distributed in both gases. The most probable value, however, is 2·00245.

This value, combined with the value 15·882 for the ratio of the densities found by Lord Rayleigh, gives for the atomic weight of oxygen

$$15\cdot862$$

$$\begin{array}{l} \text{Dittmar and Henderson's value is. . . . } 15\cdot866 \\ \text{Cooke and Richards' } \quad \quad \quad \text{,,} \quad \text{. . . . } 15\cdot869 \end{array}$$

Leduc\* found for the ratio of the volumes, by taking the density of electrolytic gas from strong potassium hydrate solution and his own values for the densities of hydrogen and oxygen,

$$2\cdot0037,$$

and for the ratio of densities  $15\cdot905,$

giving for the atomic weight of oxygen,

$$15\cdot876.$$

Morley's experiments† are objected to on the ground that his apparatus is too complicated, his measuring vessel far too wide for accurate measurement and to its being used also as the explosion tube, the transferring of his gases from one mercury trough to another, and

\* 'Comptes Rendus,' vol. 115, p. 313.

† 'Amer. Journ. Science,' vol. 41, Ser. 3, pp. 220, 276.

his giving no means of saturating the gases with aqueous vapour. He further measures his pressures to 1/200th of a millimetre. His ratio for the volumes is given as

$$2\cdot00023,$$

or only 1/10th of the difference from 2·0 exactly of that found by the above-described experiments.

II. "On the Densities of the Principal Gases." By LORD RAYLEIGH, Sec. R.S. Received March 4, 1893.

In former communications\* I have described the arrangements by which I determined the ratio of densities of oxygen and hydrogen (15·882). For the purpose of that work it was not necessary to know with precision the actual volume of gas weighed, nor even the pressure at which the containing vessel was filled. But I was desirous before leaving the subject of ascertaining not merely the relative, but also the absolute, densities of the more important gases, that is, of comparing their weights with that of an equal volume of water. To effect this it was necessary to weigh the globe used to contain the gases when charged with water, an operation not quite so simple as at first sight it appears. And, further, in the corresponding work upon the gases, a precise absolute specification is required of the temperature and pressure at which a filling takes place. To render the former weighings available for this purpose, it would be necessary to determine the errors of the barometers then employed. There would, perhaps, be no great difficulty in doing this, but I was of opinion that it would be an improvement to use a manometer in direct connexion with the globe, without the intervention of the atmosphere. In the latter manner of working, there is a doubt as to the time required for full establishment of equilibrium of pressure, especially when the passages through the taps are partially obstructed by grease. When the directly connected manometer is employed, there is no temptation to hurry from fear of the entrance of air by diffusion, and, moreover (Note A), the time actually required for the establishment of equilibrium is greatly diminished. With respect to temperature, also, it was thought better to avoid all further questions by surrounding the globe with ice, as in Regnault's original determinations. It is true that this procedure involves a subsequent cleaning and wiping of the globe, by which the errors of weighing are considerably augmented; but, as it was not proposed to experiment further with hydrogen, the objection was of less force. In the case of the heavier

\* 'Roy. Soc. Proc.' February, 1888; February, 1892.

